AD No. 33 908
ASTIA FILE COPY
A+B

Contract No. N6-ori-02026

Project No. NR 052 183

Eighth Technical Report

OXYGEN ATOM TRANSFER PROCESSES

June 1954

Henry Taube
University of Chicago
Department of Chemistry

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

DISTRIBUTION LIST

No. of Copies	Addressee
1	Commanding Officer Office of Naval Research Branch Office 150 Causeway Street Boston, Massachusetts
2	Commanding Officer Office of Naval Research Branch Office John Creror Library Building 10th Floor, 86 East Randolph Street Chicago 1, Illinois
1	Commanding Officer Office of Naval Research Branch Office 364 Broadway New York 13, New York
1	Commanding Officer Office of Naval Research Branch Office 1000 Geary Street San Francisco 9, California
1	Commanding Officer Office of Naval Research Branch Office 1030 North Green Street Pasadena 1, California
2	Officer-in-Charge Office of Naval Research Branch Office Navy Number 100 Fleet Post Office New York, New York
6	Director, Naval Research Laboratory Washington 25, D.C. Attention: Technical Information Officer
2	Chief of Naval Research Office of Naval Research Washington 25, D.C. Attention: Chemistry Branch
1	Dr. Ralph G.H. Siu, Research Director General Laboratories, QM Depot 2800 South 20th Street Philadelphia 45, Pennsylvania
1	Dr. Warren Stubblebine, Research Director Chemical and Plastics Section, RDB-MPD Quartermaster General's Office Washington 25, D.C.

DISTRIBUTION LIST - PAGE 2

No. of Copies	Addressee
1	Dr. A. Stuart Hunter, Technical Director Research and Development Branch MPD Quartermaster General's Office Washington 25, D.C.
1	Research and Development Group Logistics Division, General Staff Department of the Army Washington 25, D.C. Attn: Dr. W.T. Read, Scientific Adviser
2	Director, Naval Research Laboratory Washington 25, D.C. Attention: Chemistry Division
2	Chief of the Bureau of Ships Navy Department Washington 25, D.C. Attention: Code 340
2	Chief of the Bureau of Aeronautics Navy Department Washington 25, D.C. Attention: Code TD-4
2	Chief of the Bureau of Ordnance Navy Department Washington 25, D.C. Attention: Code Rexd
1	Dr. H.A. Zahl, Technical Director Signal Corps. Engineering Laboratories Fort Monmouth, New Jersey
1	Dr. A. Weissler Department of the Army Office of the Chief of Ordnance Washington 25, D.C. Attention: ORDTB-PS
1	U.S. Naval Radiological Defense Laboratory San Francisco 24, California Attention: Technical Library
1	Naval Ordnance Test Station Inyokern CHINA LAKE, California Attention: Head, Chemistry Division

No. of Copies	Addressee
1	Office of Ordnance Research 2127 Myrtle Drive Durham, North Carolina
1	Technical Command Chemical Corps. Chemical Center, Maryland
1	U.S. Atomic Energy Commission Research Division Washington 25, D.C.
1	Brookhaven National Laboratory Technical Information Service Upton L.I., New York Attention: Research Library
1	U.S. Atomic Energy Commission Library Branch, Technical Information, ORE Post Office, Box E Oak Ridge, Tennessee
1	Dr. Wendell M. Latimer Department of Chemistry University of California Berkeley, California
1	Dr. J.I. Hoffman Chemistry Division National Bureau of Standards Washington 25, D.C.
1	Dr. A.E. Martell Department of Chemistry Clark University Worcester 3, Massachusetts
1	Argonne National Laboratory Post Office Box 299 Lemont, Illinois Attention: Dr. Hoylande D. Young
1	U.S. Atomic Energy Commission 1901 Constitution Avenue, N.W. Washington 25, D.C. Attention: B.M. Fry

No. of Copies	Addressee
1	Brookhaven National Laboratory Information and Publications Division Documents Section Upton, New York Attention: Miss Mary E. Waisman
1	Carbide and Carbon Chemicals Division Plant Records Dept., Central Files(K-25) Post Office Box P Oak Ridge, Tennessee
1	Carbide and Carbon Chemicals Division Central Reports & Information Office(Y-12) Post Office Box P Oak Ridge, Tennessee
1	General Electric Company Technical Services Division(Info.Group) Post Office Box 100 Richland, Washington Attention: Miss M.G. Freidank
1	Iowa State College Post Office Box 144, Station A Ames, Iowa Attention: Dr. F.H. Spedding
1	Knolls Atomic Power Laboratory Post Office Box 1072 Schenectady, New York Attention: Document Librarian
1	Mound Laboratory U.S. Atomic Energy Commission Post Office Box 32 Miamisburg, Ohio Attention: Dr. M.M. Haring
1	Oak Ridge National Laboratory Post Office Box P Oak Ridge, Tennessee Attention: Central Files
1	Los Alamos Scientific Laboratory Post Office Box 1663 Los Alamos, New Mexico Attention: Document Custodian

No. of Copies	Addressee
1	U.S. Atomic Energy Commission New York Operations Office Post Office Box 30, Ansonia Station New York 23, New York Attention: Division of Technical Information and Declassification Service
1	U.S. Atomic Energy Commission Library Branch, Technical Information, ORE Post Office Box E Oak Ridge, Tennessee
1	University of California Radiation Lab. Information Division Room 128, Building 50 Berkeley, California Attention: Dr. R.K. Wakerling
1	University of Rochester Atomic Energy Project Post Office Box 287, Station 3 Rochester 7, New York Attention: Technical Report Control Unit
1	Western Reserve University Atomic Energy Medical Research Project Room 365, School of Medicine Cleveland 6, Ohio Attention: Dr. H.L. Friedell
1	Westinghouse Electric Corporation Atomic Power Division Post Office Box 1468 Pittsburgh 30, Pennsylvania Attention: Librarian
5	ASTIA Document Service Center Knott Building Dayton 2, Ohio
1	Office of Technical Services Department of Commerce Washington 25, D.C.
1	Office of Secretary of Defense Pentagon, Room 3D1041 Washington 25, D.C. Attention: Library Branch (R & D)

No. of Copies	Addressee
1	Dr. A.G. Horney Office Scientific Research R and D Command USAF Box 1395 Baltimore, Maryland

AD No. 33 908-A
ASTIA FILE COPY

[Reprinted from the Journal of the American Chemical Society, 76, 2099 (1954).]

Tracer Studies on the Decomposition of Ozone in Water

By Otto L. Forchheimer and H. Taube

[Reprinted from the Journal of the American Chemical Society, **76**, 2099 (1954).]
Copyright 1954 by the American Chemical Society and reprinted by permission of the copyright owner.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO

Tracer Studies on the Decomposition of Ozone in Water

BY OTTO L. FORCHHEIMER AND H. TAUBE

RECEIVED DECEMBER 11, 1953

The direct exchange of O_3 with water in acid solution is very slow; however, exchange does take place to a limited extent when decomposition occurs. The exchange induced on decomposition is inhibited by Cl^-, HOAc and HNO_3 (at high concentration), but is the same in dilute $HClO_4$, HNO_3 or H_2SO_4 solution, and is the same for the hydrogen peroxide induced and the spontaneous decomposition. The extent of exchange increases as O_3 concentration decreases, to a value equivalent to the exchange of $^1/_6$ of the oxygen of the ozone decomposed. These results, in particular the extent of exchange, demonstrate hydroxyl radical as the exchange and decomposition active intermediate for the non-inhibited reactions. In alkaline solution, the exchange of ozonized oxygen and water under some conditions is greater than can be accounted for by the exchange of all the ozone decomposed; ozone catalyzes or induces the exchange of O_2 with water in alkali.

The hydroxyl radical has been proposed as an intermediate in a great variety of reactions in water solution.[1] While it is likely that this species is actually involved in many of the systems, in no case has proof been advanced that the intermediate carrying the bulk of the reaction is really the hydroxyl radical. The ubiquitous nature of the radical derives from the simple chemistry relating it to water, hydrogen peroxide and ozone, the difficulty of characterizing it from its high reactivity. It apparently reacts with a wide variety of substances, whether reagents or impurities in them, and even with rather inert reducing agents such as Cl^- and HOAc.[2] The general ambiguity about mechanisms involving it centers around the question of whether a particular powerful oxidizing intermediate under study is the hydroxyl radical, or an intermediate generated by the reaction of hydroxyl radical with some substance in the solution. Thus in the work on the decomposition of ozone induced

---

(1) N. Uri, *Chem. Revs.*, **50**, 375 (1952).

(2) H. Taube and W. C. Bray, THIS JOURNAL, **62**, 3357 (1940).

by hydrogen peroxide, the presence of a powerful $1e^-$ oxidizing agent has been demonstrated.[2] However, kinetic differences in the system are produced by substituting the acids $HClO_4$, HNO_3, H_2SO_4 for each other, which show that at least two of the corresponding anions exert specific effects. Hence the question arises in each case, whether any hydroxyl radical formed may not react with the acid anion, so that the oxidizing intermediate studied is in part at least a species derived from the anion.

A reaction which offers some hope of distinguishing between HO and other radicals is the exchange of the oxygen of the radical with water.[3] In the work reported here, we have attempted to find evidence for the participation of HO in reactions of O_3 in water solution by measuring the extent of the exchange[3] which occurs when O_3 is decomposed in water of different isotopic composition. An important difference between HO and the radicals which may be formed by it, or rival oxygen radicals which might be assumed, is the extent of the exchange which each can induce. The advantage which ozone chemistry offers for the purpose at hand over that of hydrogen peroxide, is that here the hydroxyl is converted to the product O_2 which under usual conditions does not exchange with water, while in the reaction with hydrogen peroxide it is presumably converted to water

$$HO^* + HOOH \longrightarrow H_2O^* + HO_2$$

Reference has been made in the literature to an attempt by E. Collinson and F. S. Dainton[4] to find evidence for the exchange of hydroxyl and water, examining the oxygen liberated when H_2O_2 decomposes in water of different oxygen isotopic composition. No unique conclusion can be drawn from the failure to observe exchange using this approach. A number of causes, in addition to slowness of the exchange in question might be responsible for the failure to observe isotope mixing of the oxygen derived from H_2O_2 with the solvent.

Experimental

Procedure.—Ozonized oxygen was prepared from highest purity tank oxygen by passing the dried gas through a standard type of ozonizer. The ozonizers were of Pyrex glass; on cooling in Dry Ice–acetone, they delivered 8% O_3 in the gas stream, this concentration being sufficient for our purposes. Lower concentration levels were maintained by allowing the ozonizer to operate at room temperature or by increasing the flow rate.

Three types of reaction have been studied, the spontaneous decomposition in acid solution, the induced decomposition in acid and the spontaneous decomposition in alkaline solution. In all experiments, cells were used providing about 25 ml. of gas space for 5 ml. of solution. The reaction cells were filled by passing ozonized oxygen through the solution from which only the inducing agent was omitted, until air was completely swept out. The initial concentration of ozone in the gas was determined by analyzing the contents of a dry bulb in series with the reaction vessel. The gas mixtures in contact with alkaline solution were left to proceed to complete decomposition. Those in contact with acid solution usually contained residual ozone at the time of analysis. In these experiments, two or three separate reaction bulbs were prepared, of which one was used to yield the value of the ozone concentration at the time of analysis, and the remaining one or two were used for mass spectrometric determination of the isotope ratio of the gas. During reaction the cells were stored in the dark at 23 ± 1°, and were subjected to a gently rocking motion for stirring.

The ozone was analyzed by passing the gas carried by a stream of air through neutral potassium iodide solution, and determining the liberated iodine with standard thiosulfate. In all experiments the solution was enriched in O^{18}, and the gas was of normal isotopic composition. The isotopic composition of the solutions was estimated, knowing that of the enriched water, and taking account of the exchangeable oxygen added. The isotopic composition of the ozonized oxygen was determined by drying the gas, decomposing the ozone by heat, and analyzing the oxygen in a mass spectrometer. Any samples showing abnormally high N_2 peaks were rejected. It should be noted that no errors are introduced due to fractionation, except for the experiments in which an inducing agent is present. In these, a small fraction of the ozone oxygen is converted to water. However, even here, the effects due to fractionation can be only a small fraction of those observed due to exchange, and will affect the over-all isotope ratio only in the 5th significant figure. The initial isotopic composition of the ozonized oxygen was determined by passing the gas through water of normal isotopic composition, and making the determination on the washed gas. Gas so treated invariably yielded a slightly lower value for the ratio O^{18}/O^{16} than dry gas. The reason for the difference is not known, but may be caused by a spurious component of mass 34 which is removed by the ozonization and washing. Mass spectrometer analyses requiring high precision, as in experiments with gas containing the lowest concentrations of ozone, were made on an instrument made available through the courtesy of Prof. H. C. Urey, giving a precision of 2 parts in 10^4 in the isotope ratio.

Reagents were A.R. grade. The enriched water used as reaction medium was purified by distillation from alkaline permanganate, and redistillation, using all-glass stills. Other work[2] has shown the sensitivity of the rate of decomposition of ozone to the presence of impurities even at low concentration. This factor, more than the analyses, limits the precision of the data we have obtained. Particularly when as in the experiments in acid, extent of decomposition and mass spectrometer analyses are performed on separate samples, on occasion a wildly aberrant result was obtained, attributable to an accidental impurity in one of the samples. Most of the conclusions are based on experiments for which the results have been confirmed, or for an array of data which show a systematic relation to the variation of some parameter. Apparently the grease used for the stopcocks (Halocarbon product) is without effect; no difference in behavior was noted between experiments in which the solution was in direct contact with greased seals, or those conducted by isolating the seal at the end of a tube opening to the gas phase. Ordinary stopcock greases gave very erratic results, and experiments in tubes lubricated with them showed much smaller values of the extent of exchange. The reaction vessels were cleaned with concentrated nitric acid after removing the grease with solvent, rinsed thoroughly, finally with redistilled water, and dried in an oven at 110°.

The data were treated, taking account of the change in isotopic composition of the total gas, the enrichment of the water and the amount of ozone decomposed, by calculating the fraction (X) of ozone decomposed which exchanged with the solvent to produce the observed enrichment. For induced reactions, two changes take place: net decomposition of ozone and the stoichiometric reaction of O_3 with the inducing agent. Only the ozone undergoing net decomposition was used in calculating X. The theoretical justification is that HO which reacts with the inducing agent forms water and thus does not contribute to the exchange; the empirical justification is that only on this basis are the results concordant and meaningful.

Results

Table I shows the results of the experiments in acid solution, both induced and spontaneous, Table II, for the decomposition in alkaline solution.

Discussion

In the absence of decomposition (compare results of experiments 1.11, 1.12, 1.21 and 1.22 with others)

---

(3) O. L. Forchheimer and H. Taube, THIS JOURNAL, **74**, 3705 (1953).

(4) F. S. Dainton, *Ann. Reports*, **45**, 37 (1948).

TABLE I

THE EXCHANGE OF O_3 ON DECOMPOSITION IN ACID SOLUTION

(Temp., 23 ± 1°; total pressure of gases, 760 mm., except in 1.33–1.35. N_t/N_0 represents the change in the ratio O^{18}/O^{16} on decomposition; solution 7.0- to 7.3-fold enriched in O^{18}.)

No.	Time, hr.	Inducing agents[e] and catalysts	Medium	p_{O_3}, mm.	Δp_{O_3}	N_t/N_0	X
1.11	67	3.3×10^{-3} *M* Cl^-	0.04 *M* $HClO_4$	38	7.0	1.000	....
1.12	108	3.3×10^{-3} *M* Cl^-	.04 *M* $HClO_4$	36	10.5	1.002	....
1.13	80	....	.04 *M* $HClO_4$	37	21.2	1.029_5	0.12[a]
1.14	88	....	.04 *M* $HClO_4$	36	24.5	1.027	$.09_5$[a]
1.21	17	3.3×10^{-3} *M* Cl^- 1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	33	8.5	1.000[b]	....
1.22	7½	1×10^{-3} *M* HOAc 1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	33	9.9	1.002[b]	....
1.31	16	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	8.4	6.4	1.045[b] 1.0045[b]	.15 .15
1.32	22	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	8.4	6.6	1.0070[b]	.21
1.33	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	8.4	4.9	1.012	.16[c]
1.34	18	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	13	8.6	1.027	.13[c]
1.35	18	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	13	6.4	1.017	.14[c]
1.36	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	17	11.6	1.013	.17
1.37	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	33	21.3	1.024	.13
1.38	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	36	21.3	1.031	.15
1.39	16	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	52	41.5	1.042	.10
1.40	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	58	47.6	1.040 1.045	.090[d] .096[d]
1.51	17	1×10^{-3} *M* H_2O_2	.04 *M* $HClO_4$	32	25.0	1.034 1.033	.13 .13
1.52	17	1×10^{-3} *M* H_2O_2	.17 *M* $HClO_4$	25	13.6	1.021	.18
1.53	18	1×10^{-3} *M* H_2O_2	.35 *M* $HClO_4$	34	9.8	1.011 1.007_0	.22 .14
1.54	17	1×10^{-3} *M* H_2O_2	.035 *M* HNO_3	28	20.5	1.017 1.021	.09 .11
1.55	18	1×10^{-3} *M* H_2O_2	.35 *M* HNO_3	28	6.5	1.000+	<.01
1.56	18	1×10^{-3} *M* H_2O_2	.02 *M* H_2SO_4	33	20.5	1.020 1.033	.11 .18
1.61	8	1×10^{-4} *M* HCOOH	.04 *M* $HClO_4$	43	10.0	1.000	<.01
1.62	9	1×10^{-3} *M* HCOOH	.04 *M* $HClO_4$	37	11.4	1.007	.08

[a] Calculated by subtracting from the decomposition the residual decomposition observed over the same time interval in the chloride inhibited reaction. This residual decomposition does not produce exchange, and presumably involves a different, possibly heterogeneous path. [b] Analysis made using the precise mass spectrometer. [c] Total pressure ¼ usual. [d] Contact with grease only in gas phase. [e] Complete consumption H_2O_2 and HCOOH.

the exchange of O_3 with water in acid solution is very slight. The exchange observed is therefore coupled to the decomposition, presumably by some intermediate which is a catalyst for the decomposition. The most definite evidence about the nature of the intermediate responsible comes from the measurement of the limiting extent of exchange at low ozone concentration. Owing to the imprecision of the data, an exact value for the limiting exchange has not been established, but the data show that of chemically reasonable values as simple fractions, a limit of $^1/_6$ fits the data best. This is the value expected with HO as the intermediate responsible. The following reaction scheme, which incorporates reactions previously discussed for the catalysis by HO of the decomposition of O_3[2,5] and a step for the exchange of HO and H_2O, is consistent with the exchange data.

$$HO + H_2O^* \longrightarrow HO^* + H_2O \quad (1)$$

$$HO^* + O_3 \longrightarrow HOO^* + O_2 \quad (2)$$

$$HOO^* + O_3 \longrightarrow HO + OO^* + O_2 \quad (3)$$

$$\text{Net:}\ H_2O^* + 2O_3 \longrightarrow 2O_2 + OO^* + H_2O.$$

In this scheme, reaction 3 is visualized as H atom or electron transfer (HO_2 is apparently a fairly strong acid)[6] rather than an oxygen atom transfer process. In view of the strength of the O–O bond in HO_2, such a mechanism seems more likely than O atom transfer to O_3. Since the extent of exchange in acid is independent of O_2 pressure (*cf.* experiments 1.33–1.35 and expts. 1.31–1.32) the effect is not caused by an intermediate catalyzing the exchange of O_2 and water; similarly the dependence on O_3 concentration, the exchange increasing as O_3 decreases, shows that it is not caused by catalysis of O_3–H_2O exchange. Rather, the maximum extent of the exchange is a direct measure of the number of atoms of exchangeable oxygen converted to O_2, which is offered by the intermediate over the catalytic cycle. The mechanism proposed satisfies the kinetic requirements outlined. Other intermediates have been considered. With HO_2 or HO_3 assumed as the exchangeable intermediate, the limiting value of extent of exchange in each case is expected to be $^1/_3$. The mechanism with HO_3

---

(5) J. Weiss, *Trans. Faraday Soc.*, **31**, 668 (1935).

(6) H. Taube, THIS JOURNAL, **64**, 2368 (1942).

TABLE II

EXCHANGE OF OZONIZED OXYGEN AND WATER IN ALKALINE SOLUTION

Temp., 23 ± 1°; decomp. O_3 complete in all expts.; time variable, of the order of hours).

No.	NaOH, M	Special conditions	p_{O_3}, mm.	N_α/N_0	X
2.01	0.00031	....	27.5	1.016	0.04_6
2.03	.0010	....	35.0	1.271	.71
				1.297	.77
2.03	.0050	....	32.6	1.816	2.3
				1.860	2.4
2.04	.0055	....	31.1	1.756	2.1
				1.642	1.8
2.05	.0055	2.5×10^{-3} M Cl^-	28.1	1.627	2.1
				1.699	2.3
2.06	.0050	8×10^{-4} M H_2O_2	31.1	1.621	1.9
				1.655	2.0
2.07	.0055	p_{O_2} reduced to $^1/_4$	6.5	1.462	1.6
				1.442	1.5
2.08	.0055	....	12.9	1.424	2.9
				1.389	2.7
2.09	.092		31.9	2.548	4.4
				2.941	5.5
2.10	.092		22.1	2.651	6.8
2.11	1.03		30.4	1.878	2.7
				2.097	3.6
2.12	9.53		34.2	1.079	0.21
				1.079	0.21
2.13	10.15		22.0	1.075	.30
				1.062	.25

can be formulated as

$$HO_2 + 2H_2O^* \longrightarrow HO^*OO^* + 2H_2O$$
$$HO^*OO^* + O_3 \longrightarrow HO^*O + O^*O + O_2$$
$$HO^*O + O_3 \longrightarrow OO^* + HO_2$$

The limiting exchange to be expected with ClO_4 as the active intermediate cannot be arrived at as definitely as for the oxygen radicals considered. The most likely value is zero. If the radical ClO_4 retains substitution properties of ClO_4^-, it would be expected to be rather inert with respect to oxygen exchange; furthermore, even if ClO_4 did exchange oxygen with solvent, the Cl–O bond would have to be severed in some step to bring this oxygen into the gas phase. Of greater force in rejecting ClO_4 as the responsible intermediate in $HClO_4$ solution, is the experimental observation that in HNO_3, $HClO_4$ and probably H_2SO_4 solution, at least at low concentration, the extent of the exchange is nearly the same. Of the reasonable intermediates, HO is the only one that explains the exchange data and in this sense the observations on exchange constitute proof of the participation of HO in the catalytic decomposition of O_3 in water.

The interpretation advanced brings many of the additional observations immediately into line with the kinetic work on chain reactions in mixtures of H_2O_2 and O_3.[2] Foremost is the effect of Cl^- and HOAc, which inhibit both the net reaction of H_2O_2 and O_3, and the decomposition of O_3 induced by it; the exchange, which also depends on the presence of HO, is also strongly inhibited. Other paths exist for the decomposition of O_3, as at high inhibitor concentration, which presumably do not involve HO as the intermediate attacking O_3.[2] These paths are observed not to produce O_2 exchange on decomposition. At high nitrate ion concentration in acid, the exchange is also wiped out, although the decomposition is not; the kinetic data[2] also indicated reaction of the oxidizing intermediate generated by $O_3 + H_2O_2$ with some (or all) of the anions ClO_4^-, NO_3^-, $SO_4^=$. The concentration of $SO_4^=$ was not increased sufficiently in the present work to make a rigorous test of the efficiency of the reaction of HO and $SO_4^=$. Formate ion, shown by kinetic evidence[7] to yield the same intermediate for the decomposition of O_3 as does H_2O_2, also induces exchange. The conditions of the kinetic experiments and those of the exchange experiments were not identical (higher temperature and lower (O_3) in the exchange work) but the indications from the exchange results are that at higher HCOOH concentration, HO is indeed the principal catalyst for the induced decomposition of O_3. Here as in the kinetic work, the remarkable result appears that the HO chain for O_3 is supplanted by some other path, presumably involving a carbon radical, at *low* (HCOOH).

The observation made in the kinetic work that the rates of the H_2O_2 induced and the spontaneous decompositions of O_3 are sensitive to the same inhibitors indicated the conclusion that the reactions proceed by a common path. This conclusion is confirmed by the exchange results which show that the extent of exchange is very nearly the same by both paths. Thus, some mechanism exists for generating HO from O_3 in water, the HO then catalyzing the decomposition of O_3. However, other paths also operate for the spontaneous decomposition, probably including heterogeneous ones, which are not sensitive to Cl^- or HOAc, and do not cause the exchange of O_3 on decomposition.

The exchange results afford some entirely new conclusions about the properties of the hydroxyl radical. The decrease in the extent of exchange as the concentration of O_3 increases makes possible an estimate of the relative specific rate of exchange, and the reaction with O_3. The average value of O_3 concentration (average computed from mean value of the log (O_3)) in expt. 1.40, is 24 mm., corresponding to a concentration in solution of 3.1×10^{-4} M. This concentration of O_3 suffices to reduce X from the maximum value of 0.166 to 0.09_3. The rates of exchange and of reaction with O_3 for the experiment are in the ratio 0.093/0.073, and taking account of the ozone concentration, the corresponding specific rate ratio k_1/k_2, is 4×10^{-4}. Thus quite a low concentration of O_3 suffices to wipe out the exchange effect completely. The relative specific rate of reaction of HO with H_2O_2 as compared to O_3 is 0.32 (at 0°),[2] hence a fairly low concentration of H_2O_2 also competes effectively against exchange. The data on the variation of X with concentration of $HClO_4$ indicate no effect in the range 0.004 to 0.04 M, but indicate an increase at higher acid. The increase presumably means that the competition between exchange and reaction with O_3 is more favorable to exchange at higher acid. An explanation for this behavior is that the exchange path at low acid involves HO + H_2O, but that at higher acid, the path

[7] H. Taube, THIS JOURNAL, 63, 2453 (1941).

$H^+ + OH + H_2O \rightarrow$ also becomes important. It is possible that the mobility of HO is greatly increased at high acid, because of the opportunity a complex of formula H_2O^+ affords for the radical to move by electron transfer in the water lattice.

The most interesting observation made in the experiments in alkaline solution is that X in these solutions can exceed unity. This means that not only the oxygen formed by the ozone decomposed, but also additional oxygen is brought into isotopic equilibrium with the solution. The means by which the exchange occurs is not known. The qualitative kinetic observations: that the extent of exchange diminishes both at high alkali and low alkali, that it increases as the pressure of oxygen increases, and that the turnover of oxygen per molecule of ozone increases as the ozone concentration decreases are compatible with a mechanism in which an intermediate formed on the decomposition of O_3 catalyzes the exchange of OH^- and O_2. A possibility is that the hydroxyl radical ion is the intermediate in question. In alkaline solution, HO, which can be expected to lose a proton in approximately the same range of acidity as H_2O_2, will be present at least in part as O^-. The exchange of hydroxyl with water (and therefore of O^-) already has been demonstrated. The exchange of O^- and oxygen may occur *via* the reaction $O^- + O_2 = O_3^-$. The ion O_3^- is known to be formed on the reaction of O_3 and solid KOH, and has been characterized in the solid state.[8] A distinct mechanism for the exchange, in which O_3 engages in a reversible reaction with OH^-, analogous for example to the reaction of SO_2 and OH^-, also fits the observations made thus far, except possibly the dependence of exchange on (O_2). A simple means of distinguishing the two modes of action would be that followed in acid solution, to study inhibition of the exchange. Experiments of this type performed thus far lead to no definite conclusion. The failure of Cl^- to inhibit the exchange does not rule out the O^- mechanism.[9] The couple $OH^- = HO + e^-$, $E^0 = -1.9$, is not sufficiently powerful to oxidize Cl^- to Cl. If HO is further stabilized by the change $HO + OH^- = H_2O + O^-$, the oxidation becomes even less favorable. If a value of 10^{-10} is assumed as the dissociation constant of HO, E^0 for the principal couple in alkaline solution: $2OH^- + H_2O + e^-$ is -1.6 volt. Neither equilibrium nor mechanism favor a rapid reaction of O^- and Cl^-. The single experiment with H_2O_2 and O_3 merely confirms an observation which can be made more directly, that H_2O_2 and O_3 react rapidly in alkaline solution. An O^- mechanism has been proposed for the γ-ray induced chain exchange of O_2 and water in alkaline solution.[10] It is likely that the intermediate causing the catalysis in this system and that studied by us is the same. But also for the radiation induced reaction, no observations are published that definitely rule out catalysis by O_3 which may be produced at low concentration, as the cause of the exchange.

Acknowledgments.—The authors wish to acknowledge the generous help of Dr. George Edwards in making the isotope analyses using the precise mass spectrometer. The research was supported by the Office of Naval Research under contract N6-Ori-02026. The funds for the purchase of the mass spectrometer used for most of the analyses were supplied by the Atomic Energy Commission under contract At(11-1)-92.

CHICAGO, ILLINOIS

---

(8) I. A. Karzarnovskii, B. P. Nikolski and T. A. Abletsova, *Doklady Akad. Nauk. S.S.S.R.*, **64**, 69 (1949).

(9) The report (Paper 126, Division of Physical and Inorganic Chemistry, 123rd meeting, ACS, Los Angeles, March, 1953) that Cl^- does inhibit was wrong.

(10) E. J. Hart, S. Gordon and D. A. Hutchison, THIS JOURNAL, **74**, 5548 (1952).

AD No. 32 908
ASTIA FILE COPY

[Reprinted from the Journal of the American Chemical Society, 76, 2103 (1954).]

Evidence for a Bridged Activated Complex for Electron Transfer Reactions

By Henry Taube and Howard Myers

[Reprinted from the Journal of the American Chemical Society, **76**, 2103 (1954).]

Copyright 1954 by the American Chemical Society and reprinted by permission of the copyright owner.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES, UNIVERSITY OF CHICAGO]

Evidence for a Bridged Activated Complex for Electron Transfer Reactions

BY HENRY TAUBE AND HOWARD MYERS

RECEIVED NOVEMBER 9, 1953

The reaction of Cr^{++} with a variety of ions of the type $Co(NH_3)_5X^{++}$ as oxidizing agent takes place with quantitative transfer of X to the reducing agents. For the system with $X^- = Cl^-$, it has been shown that the transfer takes place without there being any exchange with chloride ion in solution. These observations lead to the conclusion that the activated complexes for the electron transfer reactions in question have configurations in which X makes a bond simultaneously to Cr and to Co. Any group which has unpaired electrons available for interaction with Cr^{++} is found to provide a more accessible pass for electron transfer than does the proton coördination shell of $Co(NH_3)_6^{+++}$. A bridged activated complex also explains observations made on reactions of Cr(III) complexes catalyzed by Cr^{++}. Results obtained with other oxidizing agents which are substitution-inert show that although formation of a bridged activated complex does take place, *net* transfer of the bridging group from oxidizing agent to reducing agent is not an essential feature of the electron transfer process. Strong evidence is presented in support of the view that a bridged activated complex is involved also in the action of substitution-labile oxidizing agents containing Fe(III) on Cr^{++} (or in the "catalysis" of the reaction of Cr^{++} and Fe^{+++} by anions), and in the exchange of electrons between Fe^{++} and Fe(III) species.

The formulas of most aquo ions in water are not known, and therefore the problem of the mechanism of oxidation–reduction reactions involving them goes particularly deep. Furthermore, nothing is known about the changes in the coördination spheres which may accompany electron transfer, although such information is essential to the description of the electron transfer process. Information of this kind is difficult to obtain for all but a few aquo ions, the few comprising those which yield substitution-inert products on undergoing electron transfer. The reducing agent Cr^{++} qualifies for an investigation of the kind implied. The results of a study of the products formed when it is oxidized by various agents forms the subject of the present report.[1] Although Cr(II) is labile to substitution, most of the product complexes containing Cr(III) in acid solution preserve their identity for periods of time long compared to the rate of oxidation of Cr^{++}. Thus it can often be shown that a group in question found combined with Cr(III) did not combine with it after the act of oxidation of Cr(II). In such cases the conclusion follows that the group was attached in the activated complex, and some features of the structure and composition of the activated complex are therefore given a definite description. The entry of all the groups F^-, Cl^-, Br^-, I^-, $SO_4^{=}$ into the coördination sphere of $Cr(H_2O)_6^{+++}$ is so slow under the conditions of our experiments that this route is negligible in accounting for the complex ion products observed. In fact, at the concentration of halide present in most of the experiments, the ions[2] $CrCl^{++}$, $CrBr^{++}$ and CrI^{++} are unstable with respect to $Cr(H_2O)_6^{+++}$ and X^-, and if the systems are left to reach equilibrium, the concentrations of CrX^{++} remaining are negligible in comparison to those generated by oxidation of Cr^{++}.

The conclusions drawn from the results obtained on the oxidation of Cr^{++} have this general significance. As a minimum they serve to show what kind of process can take place when an aquo cation is oxidized. By comparing kinetic properties of paths for the oxidation of Cr^{++} with those for reactions in which only substitution-labile ions are involved, the extension of the model processes to them can be justified.

Experimental Method

The apparatus for storing and dispensing the solution of Cr^{++} was similar to that described by Lingane and Pecsok.[3] The reaction flask, 500 ml. in capacity, was fitted with four ground glass entries, one to accommodate the delivery tube of the pipet, one for the mercury seal stirrer, one providing entrance and exit for gas, one for introducing reagents, and a stopcock at the bottom to serve as a drain.

The solution containing Cr^{++} was prepared by reducing chromium(III) perchlorate in 1 *M* $HClO_4$ with amalgamated Zn, and was protected from the atmosphere by passing a stream of CO_2 through the storage vessel. Solutions properly prepared developed only a trace of chloride ion even after a week at room temperature. The conditions contributing to favorable behavior were not studied thoroughly, but these are believed to be important: the zinc must be pure; it should be amalgamated lightly and should be used immediately; anions other than ClO_4^- should be avoided. The solutions of chromium(III) perchlorate were prepared by reducing $K_2Cr_2O_7$ with H_2O_2, and removing the $KClO_4$ formed. These solutions were used at 0.10 and 0.25 *M*, with equal success in generating and preserving Cr^{++}.

Most of the cobaltammine compounds were prepared by Mr. Franz A. Posey. Any modifications of standard procedures found helpful in their preparation will be described in a future publication bearing his name. $(NH_4)_2IrCl_6$ was prepared from commercial iridium chloride, by oxidation with Cl_2 in the presence of NH_4Cl in solution. Ferric perchlorate was prepared from $FeCl_3$, heating the salt with perchloric acid, and crystallizing it from this medium.

The procedure followed in the experiments was this. The solution for reaction was made up, omitting Cr^{++}, introduced into the reaction flask, and then left for periods of one-half to one hour. During this time the solution was stirred and a stream of carbon dioxide was passed through the reaction vessel. For experiments at the controlled temperature of 2.1 ± 0.2°, the vessel was surrounded by an ice-bath. The reaction was initiated by adding the solution containing Cr^{++}. Any Cr^{++} left at the end of the reaction was oxidized using H_2O_2 or $K_2Cr_2O_7$. Finally, the product solution was removed and analyzed.

Free chloride is readily separated from chloride in $CrCl^{++}$ by using Ag^+. No measurable loss of bound chloride takes place, even at room temperature, when the operation is carried out in acid solution. Chloride bound in $CrCl_2^+$ is more labile, and some loss from this complex ion takes place when excess Ag^+ is added. The presence of $CrCl_2^+$ is demonstrated by the fairly rapid postclouding which takes place after Ag^+ is added and AgCl removed by filtration. Both $CrCl^{++}$ and $CrCl_2^+$ yield Cl^- rapidly to Ag^+ at 95–100°. Loss to Ag^+ of Br^- and of I^- from chromic complexes is too rapid for a quantitative separation of free and bound halide by using this reagent. In the single experiment involving the distinction between free $SO_4^{=}$ and $SO_4^{=}$ associated with Cr^{++}, the free $SO_4^{=}$ was removed as $BaSO_4$.

The extinction of Cr^{+++} differs sufficiently from that of $Cr^{III}_{Cl^-}$, $Cr^{III}_{Br^-}$, $Cr^{III}_{I^-}$ species so that fairly accurate spectrophotometric analyses can be made. This method was the only one used for determining CrI^{++} and $CrBr^{++}$ in the presence of Cr^{+++}. The color of any Fe(III) species present was suppressed by adding concentrated phosphoric acid to the solutions for analysis. The wave length region from 750 to 600 mμ was found to be most useful in analyses, since contributions to the optical density by other colored species are relatively least here. The absorption coefficients of chromium(III) species in this wave length region are rather insensitive to fairly drastic changes in the environment, as for example changing from 2 *M* $HClO_4$ to 2 *M* HCl, which occasions at most a 2% change in the values.

The notation adopted in this paper is as follows: M^{+n} specifies an aquo ion of indicated charge; the symbol followed by a Roman numeral is used when only the oxidation state is specified; the symbol with a Roman numeral superscript, and a symbol subscript, specifies the oxidation state, and the identity but not the number of the associated ions.

The extinction coefficients tabulated are defined by the equation

$$\alpha = \frac{1}{cd}\log\frac{I_0}{I}, \text{ where } c \text{ is in moles l.}^{-1} \text{ and } d \text{ in cm.}$$

Results

A. The Reaction of Cr^{++} with Substitution-Inert Complex Ions. $Co(NH_3)_5Cl^{++}$.—A solution containing $Co(NH_3)_5Cl^{++}$ and ClO_4^- was prepared from $Co(NH_3)_5Cl_3$ by double decomposition with the requisite amount of $AgClO_4$. The reaction mixture of volume 200 ml. was 0.5 *M* in $HClO_4$ and contained 2.98 millimoles of $Co(NH_3)_5Cl^{++}$. Even at 2° the reaction with Cr^{++} takes place rapidly (the half-life is only a fraction of a minute under the conditions described), and on reaction the mixture changes from the violet-pink color of $Co(NH_3)_5Cl^{++}$ to green. Chromous ion was used in slight excess to ensure complete consumption of the reactant species containing complex-bound chloride. A negligible amount of free chloride was found at the end of the reaction, and for each mole of $Co(NH_3)_5Cl^{++}$ reduced, 0.98 mole of Cl^- was found associated with Cr(III). The complete transfer of Cl^- from $Co(NH_3)_5Cl^{++}$ to Cr^{++} was also demonstrated spectrophotometrically. The spectrum of the Cr(III) product obtained in the reaction agrees quantitatively with that of $CrCl^{++}$ prepared by an independent method (*vide infra*).

In another experiment, free chloride containing the radioactive isotope Cl^{36} was present in the reaction mixture, in molar amount twice that of $Co(NH_3)_5Cl^{++}$ and at a concentration of 0.03 *M*. The radioactivity of the chloride attached to Cr(III) after reaction was found to be 10 counts per minute above background; on complete mixing of the chloride in the system a counting rate of 2,250 per minute would have been observed.

$Co(NH_3)_5Br^{++}$.—The conditions of the reaction were the same as those described for the chloro complex. The reaction is again very rapid, seemingly more rapid than with $Co(NH_3)_5Cl^{++}$ because no delay in the consumption of Cr^{++} can be detected. In this system also, the transfer of halide to the reducing agent is essentially quantitative. This conclusion is based on the observations that no immediate precipitate forms when Ag^+ is added to the product solution obtained with $Co(NH_3)_5Br(ClO_4)_2$ as reactant[4] (although a general cloudiness begins almost at once and increases gradually) and that the spectrum of the product chromium species using $Co(NH_3)_5Br(ClO_4)_2$ or $Co(NH_3)_5Br_3$ agrees quantitatively with that of $CrBr^{++}$ prepared by the reaction of Cr^{++} and Br_2 (see Table III). The color change in the reaction of $Co(NH_3)_5Br^{++}$ and Cr^{++} is striking, because the reaction is very rapid and the intense green of the product is in marked contrast to the violet-red color of the cobaltic complex.

---

[1] Earlier communication, H. Taube, H. Myers and R. L. Rich. THIS JOURNAL, **75**, 4118 (1953).

[2] Of these ions, the most stable is $CrCl^{++}$. The equilibrium quotient $(Cr\,X^{++})/(Cr^{+++})(Cl^-)$ in a recent careful measurement by H. G. Gates and E. L. King was found to be 0.77 ± 0.06 at 4.9 μ and 74°. At the lower temperature and ionic strength of our experiments, the value of the quotient would be less, perhaps by a factor of 5 or more.

[3] J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

$Co(NH_3)_5I^{++}$.—The iodopentamminecobalt(III) was introduced as the perchlorate salt. The molar extinction coefficients of the chromic product obtained on the reaction of $Co(NH_3)_5I^{++}$ in the wave length region 850–650 mμ agreed to within 2% with the values obtained for the product of the reaction of Cr^{++} and I_2 (see Table III). Owing to the rapid release of I^- to Ag^+, the simple precipitation test for completeness of transfer is not successful in this system. However, the agreement of the spectra noted, as well as the observation that the spectra have a reasonable relation to that observed for $CrBr^{++}$, testify that transfer of iodide is also essentially complete. The reaction is again very rapid. The color of the final solution is an intense green, but the contrast with that of the reactant solution, an olive green, is not as striking as for the systems previously described.

$Co(NH_3)_5F^{++}$.—The reaction of Cr^{++} with this ion is also rapid. Quantitative data are lacking, because the sample of $Co(NH_3)_5F(ClO_4)_2$ was not very pure. The qualitative observation that the resultant solution is green-gray in color shows that at least some transfer of F^- to Cr takes place.

$Co(NH_3)_5SO_4^+$.—The results of the experiments with this ion are not as quantitative or as satisfying as those cited for the halogeno complex ions. The source of the sulfato ion was the salt $Co(NH_3)_5SO_4HSO_4 \cdot 2H_2O$. Barium perchlorate in excess of that required to precipitate the free $SO_4^=$ was added to a solution of the sulfato salt in perchloric acid. The precipitate was too fine to filter at this stage, so the reaction with Cr^{++} was carried out in the presence of $BaSO_4$ (and Ba^{++}). After reaction, the $BaSO_4$ was filtered off, though still with difficulty, and the bound $SO_4^=$ precipitated by heating and determined as $BaSO_4$. The result showed 0.87 mole $SO_4^=$ attached per mole Cr(III) formed. The major errors are in the direction to make this a lower limit for the extent of transfer. The result proves that the bulk of the reaction proceeds by transfer of $SO_4^=$, and it is possible that essentially all of it takes this path.

$Co(NH_3)_5H_2O^{+++}$.—The half-life of Cr^{++} in the presence of excess $Co(NH_3)_5H_2O^{+++}$ at 0.02 *M* in 0.5 *M* $HClO_4$ and at 25° is of the order of a minute. The rate increases as the concentration of acid is lowered, and presumably paths involving both $Co(NH_3)_5H_2O^{+++}$ and $Co(NH_3)_5OH^{++}$ operate in the acid range studied.

The reaction also was conducted with chloride ion present in the solution, then determining the amount attached in the product Cr(III). The experimental conditions were the same as those described above, except that the reactant solution was made 0.1 *M* in NaCl. The mole ratio of bound chloride to Cr(III) formed was found to be less than 0.05. Attachment of chloride to Cr(III) is not an efficient process with $Co(NH_3)_5H_2O^{+++}$ as oxidizing agent nor does there appear to be a striking catalysis of the reaction by chloride ion.

$Co(NH_3)_6^{+++}$.—The salt $Co(NH_3)_6Cl_3$ was used for this experiment, dissolved in 0.3 *M* HCl. The solubility is strongly suppressed as chloride concentration is increased so that it was necessary to work at a lower concentration level of acid. The reaction took place at room temperature, about 28°. The initial concentration of the luteo salt was 0.01 *M* and of Cr^{++}, 0.02 *M*. After 50 minutes the excess Cr^{++} was oxidized with H_2O_2 and an estimate made of the residual $Co(NH_3)_6^{+++}$ by precipitating it as the perchlorate, drying and weighing. The result showed that $Co(NH_3)_6^{+++}$ had decreased to 45% of its initial value. A rough value for the 2nd order specific rate based on this experiment is 0.7 l. mole^{-1} min.$^{-1}$.

cis-$Coen_2Cl_2^+$.—The purpose of examining the reaction of Cr^{++} with this ion was to learn whether more than one chlorine is transferred by an oxidizing agent with chlorine atoms in *cis* positions. The rate of the reaction with *cis*-$Coen_2Cl_2^+$ proved to be rapid. Only one atom was found associated with Cr(III) per equivalent of reaction. Although enough $Coen_2Cl_2^+$ was added to be in excess of the Cr^{++} (by 30%) so as to reduce the opportunity for catalysis of dissociation of $CrCl_2^+$ by Cr^{++}, the experiment must be regarded as inconclusive on the point of interest. A direct study of the relative rates in question is required, and if necessary a compound must be used which offers a more favorable relation of these rates.

$CrCl_3(s)$.—Catalysis of the dissolution of $CrCl_3$ by reducing agents has been referred to frequently.[5] In an experiment we performed, 1.610 millimoles of $CrCl_3$ was left in contact with 100 ml. of solution 0.001 *M* in Cr^{++} and 1 *M* in $HClO_4$ at room temperature for 10 minutes. During this time the dissolution of the solid was essentially complete. After quenching the reaction, the chloride associated with Cr(III) was determined and found to be 1.537 millimoles. This amount in comparison to the amount of $CrCl_3$ used shows that the net change proceeds largely to form $CrCl^{++}$ as the product. The reaction was repeated with radioactive chloride added to the solution initially. The radioactivity of the chloride found attached to Cr(III) was measured as 90 counts per minute above background; for complete exchange, 1630 counts per minute would have been observed.

$CrCl_2^+$.—The source of the dichloro complex ion was commercial green chromic chloride. Experiments on solutions of the salt using ion exchange resins[6] have shown that at least 98% of the Cr(III) is initially in the form $CrCl_2^+$. The solution used was 0.0225 *M* in the chromium (III) salt and 1 *M* in $HClO_4$. Two samples of known volume were removed at intervals, the Cr^{++} was then added, and additional samples were taken. The results of this experiment, performed at room temperature, are recorded in Table I.

TABLE I

THE REACTION OF $CrCl_2^+$ AND Cr^{++}

Sample no.	1	2	3[a]	4	5
Time,[b] min.	7	32	42	46	57
Fraction Cl^- left on Cr(III)	0.625	0.589	0.331	0.332	0.326

[a] Cr^{++} added at time = 41 min.; $(Cr^{++}) = 2.5 \times 10^{-3}$ *M*. [b] Measured from the time of dissolution.

The experiment was repeated, but at 2° and with (Cr^{++}) at 2.3×10^{-4} *M*. The record of this experiment is presented in Table II.

TABLE II

THE REACTION OF $CrCl_2^+$ AND Cr^{++}

Sample no.	1	2	3
Time after Cr^{++} added, min.	0.4	1.5	10.0
Fraction Cl^- left[a] on Cr(III)	0.436	0.338	0.334

[a] The fraction bound to Cr(III) 5 min. after dissolution was 0.622. The defect from the theoretical value for $CrCl_2^+$ of 0.667 may be caused by the direct attack of Ag^+.

Both experiments show that Cr^{++} takes $CrCl_2^+$ rapidly to the stage $CrCl^{++}$, and that further change is very much slower. The second experiment permits a rough estimate of the specific rate at 2° as of the order of 10^4 l. mole^{-1} min.$^{-1}$.

The reaction of Cr^{++} and $CrCl_2^+$ was also carried out with radioactive chloride added to the solution. A small but definite fraction of the associated chloride reaches radioactive equilibrium during the reaction. The counting rate of the associated chloride was found to be 73 per minute above background; for complete exchange 2180 per minute would have been expected. Separate experiments showed that the pick-up of radioactivity was not caused by exchange of $CrCl_2^+$ or $CrCl^{++}$ with Cl^{*-}, nor by the quenching procedure. The latter process involving slight addition of Cl^- to Cr^{++} on oxidation by H_2O_2 accounts for only a counting rate of 10 per minute above background. In an

---

(4) The compound $Co(NH_3)_5Br(ClO_4)_2$ was prepared by Mr. Paul E. Nessman.

(5) R. Abegg and Fr. Auerbach, "Handbuch der anorganischen Chemie," Vol. 4, Verlag von S. Hirzel, Leipzig, 1921, p. 76.

(6) E. L. King, private communication.

additional experiment, in which the concentration of chloride was doubled, the fraction exchanged was little altered.

Because $CrCl^{++}$ appears as a well defined stage in the reaction of Cr^{++} and $CrCl_2^{+}$, and because only a relatively small amount of Cr^{++} is needed, the reaction is a good one for developing $CrCl^{++}$ almost free from other Cr(III) species. Figure 2 shows the values of the molar extinction coefficients of $CrCl^{++}$ prepared by this method. Those obtained for $CrCl^{++}$ prepared by the reaction of $Co(NH_3)_5Cl^{++}$ and Cr^{++} differ by less than 1% in the wave length region 700 to 625 mμ.

CrI_3(s).—This compound, as anhydrous salt, was furnished through courtesy of Dr. Maurice Griffel, Iowa State University. The rate of dissolution by water is very slow but with a trace of Cr^{++} present, the reaction is much more rapid and produces an intense green color in the solution. This color is undoubtedly caused by a chromium(III)-iodide complex ion, and the behavior of the system is presumably like that of $CrCl_3$ with Cr^{++}. The complex is rapidly aquotized when the solution is warmed.

$AuCl_4^-$.—The work of Rich and Taube[7] shows that tetrachloroaurate ion undergoes substitution by H_2O and Cl^- measurably slowly. The reaction with Cr^{++} was conducted at 2° in a solution 0.5 *M* in $HClO_4$, and containing $AuCl_4^-$ in excess of that required for the oxidation of Cr^{++}. The product solution was green, but discolored by what was apparently colloidal gold. Excess Fe^{++} was added to reduce Au complexes to Au, and the free chloride was removed as AgCl. Analysis of the resulting solution showed 1.00 mole of bound Cl^- for each mole of Cr^{++} oxidized.

$Fe(CN)_6^{\equiv}$.—No quantitative observations were made on the reaction, but the qualitative observations are sufficiently striking to be worthy of record. On adding an exactly equivalent amount of Cr^{++} to a solution 0.005 *M* in $K_3Fe(CN)_6$ (and 0.01 *M* in $HClO_4$), an olive-brown precipitate formed at once and then persisted for days without apparent change. The system of the same stoichiometry arrived at by mixing $Cr(H_2O)_6^{+++}$ and $Fe(CN)_6^{----}$ is entirely different. No obvious change takes place on mixing the two ions, and the only changes noted after a time are those resulting from the gradual decomposition and discoloration of the $Fe(CN)_6^{----}$ in the air-saturated, faintly acid solution.

$IrCl_6^-$.—The reduction of $IrCl_6^-$ by Cr^{++} takes place extremely rapidly, and the end-point is easily recognizable because $IrCl_6^-$ has an intense reddish-brown color, very much more intense than that of the products. If the reaction takes place at 2°, and if Cr^{++} is added rapidly, the initial product is observed to be green in color. This color is quickly lost, and the solution then changes to a drab olive-brown shade. An attempt was made to follow the second color change spectrophotometrically. By the time of the first reading, 2 minutes after mixing, the change was almost complete, but the residual change registered suggests a half-time of *ca.* 0.5 min. for the second color change. The constitution of the final solution appears to be settled by the following observations. The extinction is the same as that of a solution made by mixing $Cr(H_2O)_6^{+++}$ and $IrCl_6^{=}$ (this ion was generated by reducing $IrCl_6^-$ with Sn^{++}). It is certain that little formation of inner sphere complex ions takes place when $Cr(H_2O)_6^{+++}$ and $IrCl_6^{=}$ are mixed, because the color adjusts to the final shade immediately on mixing, and, more convincingly, because the extinction in the range 650 mμ to 400 mμ is, except for minor variations, that calculated by adding the contributions for $Cr(H_2O)_6^{+++}$ and $IrCl_6^{=}$. Some association of the oppositely charged species does take place, for $Cr(H_2O)_6^{+++}$ is extracted somewhat less efficiently by a resin when $IrCl_6^{=}$ is present in the solution, but the product of the association is presumably an outer sphere complex ion.

B. **Reactions with Halogens.**—The results of the experiments on oxidation of Cr^{++} with halogens are related to the work reported here, because in the cases of Br_2 and I_2, the direct reactions are convenient ways of generating 1:1 chromic-halide complexes. The conditions provided for the reactions were: temperature 2°, ($HClO_4$) 1 *M*, no halide present initially (except in the case of I_2), Cr^{++} added to a solution containing the halogen in excess. Excess Cl_2 or Br_2 was removed by a stream of air, and excess I_2 in preparation for spectrophotometric measurements was reduced with SO_2.

With Cl_2 as reactant, free Cl^- is found in the solution at the end of the reaction, and only 75% of the chloride is left in association with Cr(III). The product solution obtained with Br_2 as the oxidizing agent contains practically no free bromide when tested immediately after the reaction. Evidently transfer of bromine to chromium is complete on reaction. The direct test for complete transfer fails in the Cr^{++}-I_2 reaction, but the less direct evidence tending to this conclusion already mentioned seems sufficient to establish it.

The rates of aquotization of $CrCl^{++}$ and $CrBr^{++}$ in strong acid are slow enough so that the extinctions can be measured without difficulty in a cell compartment at room temperature. With CrI^{++}, a correction must be applied for the change of extinction with time.

The ions $CrBr^{++}$ and CrI^{++} have not been prepared previously, substantially free from other Cr(III) ion species. Their extinction coefficients are recorded in Table III. $CrBr^{++}$ shows two distinct peaks in the visible region, as is characteristic of most simple complex ions of Co(III) and Cr(III).[8] The strong absorption in the ultraviolet shown by $Cr(H_2O)_6^{+++}$ moves progressively toward longer wave lengths in the series $Cr(H_2O)_5H_2O^{+++}$, $Cr(H_2O)_5Cl^{++}$, . . ., $Cr(H_2O)_5I^{++}$, and for the last named ion obscures the second peak in the visible region.

TABLE III

EXTINCTION COEFFICIENTS OF $CrBr^{++}$ AND CrI^{++}

Medium, 0.5 *M* $HClO_4$, temp. 25°

	$CrBr^{++}$ from		CrI^{++} from	
	$Cr^{++} + Br_2$	Cr^{++} + $Co(NH_3)_5$-Br^{++}	$Cr^{++} + I_2$	Cr^{++} + $Co(NH_3)_5$-I^{++}
750	0.8	0.9	3.7	3.7
700	6.2	6.2	19.9	19.8
675	11.3	11.3	30.6	30.1
650	17.1	17.2	35.7	35.4
625	19.9[a]	20.1	34.1[c]	
600	18.2		21.7	
580	14.0		16.5	
560	9.8		10.3	
540	6.0		6.4	
520	4.2		5.9	
500	4.8		9.9	
480	9.6		28.5	
460	16.6		32.1[d]	
440	22.2[b]		44.5	
420	20.6		75	
400	13.4			
380	5.7			
360	2.4			
340	5.3			
320	25.4			

[a] Max. at 622, $\alpha = 19.9$. [b] Max. at 432, $\alpha = 22.4$. [c] Max. at 644, $\alpha = 40.0$. [d] Max. at 475, $\alpha = 32.3$.

C. **Results with Labile Complex Ions as Oxidizing Agents.**—Table IV contains most of the data obtained on the formation of Cr(III)-Cl^- complexes in the oxidation of Cr^{++} by Fe(III) in the presence of chloride ion.

For a system in which paths described by the rate laws: $k_1(Fe^{+++})(Cr^{++})$, $k_H(Fe^{+++})(Cr^{++})/(H^+)$, $k_{Cl^-}(Fe^{+++})(Cr^{++})(Cl^-)$ compete, in which only the k_{Cl^-} term contributes to the formation of $CrCl^{++}$, and all the Cr^{++} reacting by this activated complex does form $CrCl^{++}$, the relation

$$\frac{Cr^{+++}}{CrCl^{++}}(Cl^-) = \frac{k_1}{k_{Cl^-}} + \frac{k_H}{k_{Cl^-}(H^+)}$$

must hold. In this relation, $(Cr^{+++})/(CrCl^{++})$ is the ratio of Cr(III) not converted to $CrCl^{++}$, compared to that which is, and (Cl^-) represents the free chloride concentration. The data in Table IV show that the function on the left is almost constant over an eightfold range in (Cl^-), but does

---

(7) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

(8) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **266**, 49 (1951).

TABLE IV

THE FORMATION OF $CrCl^{++}$ IN THE OXIDATION OF Cr^{++} BY Fe(III) IN THE PRESENCE OF Cl^-

Temp. 2°; $\mu = 2.2$

(H^+)	$(Cl^-)_i$	Av. $(Cl^-)^a$	$\frac{Cr^{+++}}{CrCl^{++}}$	$\frac{Cr^{+++}}{CrCl^{++}}(Cl^-)$	Method
0.565	0.0250	0.0233	3.90	0.091	Spec.
.565	.0500	.0467	1.90	.089	Spec.
.565	.1000	.0947	0.91	.086	Spec.
.568	.1000	.0929	0.93	.085	Grav.
2.06	.0125	.0115	4.00	.0460	Spec.
2.06	.0500	.0455	1.06	.0483	Spec.
2.06	.1000	.094	0.50	.0472	Spec.
2.06	.0250	.0222	2.28	.0484	Grav.
2.06	.0500	.0449	1.04	.0467	Grav.
2.06	.1000	.0927	0.49	.0455	Grav.

[a] Corrected for change in volume on addition of Cr^{++} (2% in the spectrophotometric experiments, 4% in the gravimetric), for the consumption of Cl^- by formation of $CrCl^{++}$, and for consumption by association with Fe^{+++}. The value of the equilibrium quotient $(FeCl^{++})/(Fe^{+++})(Cl^-) = K_{FeCl^{++}}$ under the present conditions was estimated as 1.7 by reference to the work of Rabinowitch and Stockmayer.[9]

change slightly, in the direction that at high (Cl^-), somewhat too much bound Cl^- is formed. Figure 1, which includes also data at intermediate (H^+) not reported in Table IV, shows that the variation of the function $(Cr^{+++})(Cl^-)/(CrCl^{++})$ with (H^+) follows the requirements of equation 1.

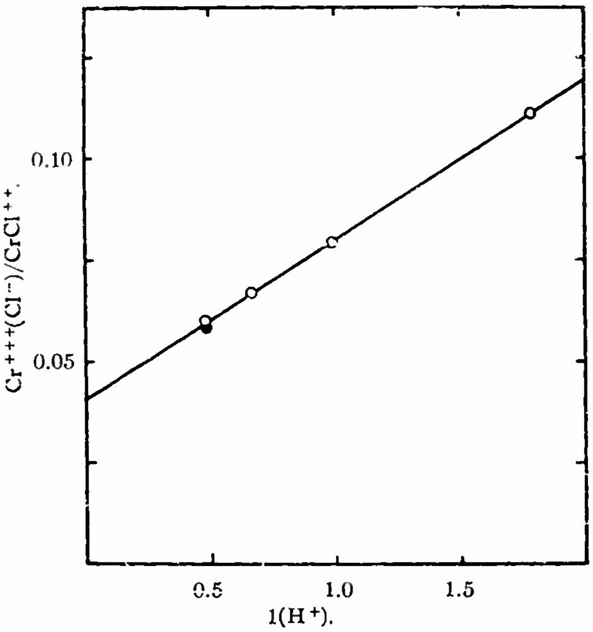


Fig. 1.—The efficiency of addition of chloride to chromium as a function of acidity: open circles, spectrophotometric data; solid circles, gravimetric data.

Experiments were also performed in media at higher concentrations of chloride ion, made up by replacing $HClO_4$ by HCl. Only the spectrophotometric method of analysis was used because the separation of free chloride from bound chloride with Ag^+ becomes inconvenient at high chloride concentration. Figure 2 shows the molar extinction coefficients for the product of the oxidation at the highest chloride concentration studied, 2 *M*, compared to the molar extinctions for $CrCl_2^+$ and $CrCl^{++}$. Applying the law for the variation of $Cr^{+++}/CrCl^{++}$ with (Cl^-) established at lower chloride concentration, it follows that less than 2% of the Cr^{++} is converted to $Cr(H_2O)_6^{+++}$ in 2 *M* Cl^-, so that only the distribution of Cr(III) between $CrCl^{++}$ and $CrCl_2^+$ need be considered. From the relation of the extinctions for the product compared to that for $CrCl^{++}$, it is evident that some species besides this ion is formed. However, the extinctions observed cannot be accounted for quantitatively by combining the $CrCl^{++}$ and $CrCl_2^+$ curves, and apparently the additional species differs from the $CrCl_2^+$ obtained from ordinary solid green chromic chloride.

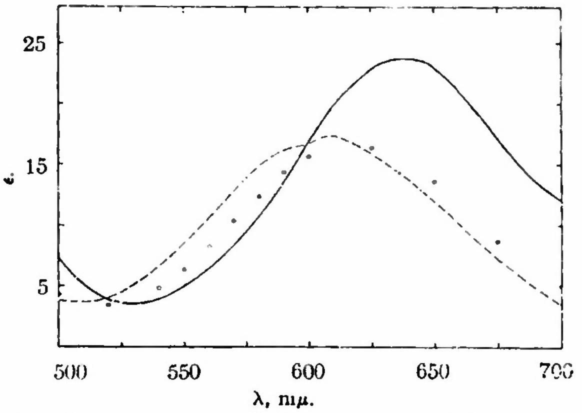


Fig. 2.—Comparison of the spectrum of the species $Cr^{III}_{Cl^-}$ produced in 2 *M* HCl with that of $CrCl^{++}$ (broken line) and $CrCl_2^+$ (solid line).

In another experiment Cr^{++} (0.25 millimole) was added to 200 ml. of solution 0.0040 *M* in $CrCl_2^+$, 0.01 *M* in Fe(III) and 1 *M* in HCl, at 2°. The extinction of the final solution was slightly less than that obtained by adding the extinctions of the product obtained in the absence of $CrCl_2^+$ to that of $CrCl_2^+$, and could be accounted for by assuming a slight net dissociation of $CrCl_2^+$ to the extent of 3.9%. The experiment proves that under the usual experimental conditions (higher Fe(III) and relatively much less $CrCl_2^+$ than in the test experiment), the consumption of Cr^{++} by Fe(III) is rapid enough so that any $CrCl_2^+$ would be largely preserved. This conclusion may not apply, however, to $CrCl_2^+$ of the kind developed by the reaction with Fe^{+++} + Cl^-, although a large difference in the rate of reaction with Cr^{++} would not be expected for the two forms. The present experiment further leads to the conclusion that the specific rate for the reaction of Cr^{++} with $Fe^{III}_{Cl^-}$ in 1 *M* HCl is four times that with $CrCl_2^+$.

The account of experiments performed on the reaction of Cr^{++} and Fe^{+++} with Br^- present appears in Table V.

TABLE V

THE FORMATION OF $CrBr^{++}$ BY THE REACTION OF Fe^{+++} AND Cr^{++} IN THE PRESENCE OF Br^-

Temp. 2.1°; $\mu = 2.2$; $(Fe(III))_0$, 0.020 *M*

(H^+)	(Br^-)	$\frac{Cr^{+++}}{CrBr^{++}}$	$\frac{Cr^{+++}}{CrBr^{++}}$
0.563	0.0736	3.92	0.289
0.563	.221	1.31	.289
1.055	.221	0.805	.182
2.07	.0242	4.10	.099
2.07	.0730	1.455	.106
2.07	.221	0.484	.107

A feature of interest is that $(Cr^{+++})(Br^-)/(CrBr^{++})$ is constant as (Br^-) varies, thus a relation of the type of equation 1 describes the dependence of the yield of complex halide on halide concentration in this system also. The general form of the variation of the yield of $CrBr^{++}$ with (H^+) is that required by equation 1. However, an important requirement of equation 1 is not satisfied by the data for Br^- and Cl^- taken together. The ratio of slope to intercept in graphs of the type of Fig. 1 should be the same for both. While the data for Br^- are not very extensive, they are sufficient to show that this condition is not fulfilled. The data in the chloride system are complete enough to establish equation 1 as a description of them, and evidently in the bromide system some additional factor enters. The qualitative behavior of the bromide system is that the path $Fe^{+++} + Cr^{++}$ is suppressed relative to $Fe^{+++} + Cr^{++} + OH^-$. A deviation of this type would be observed if a rate term $k_{HBr}(Fe^{+++})(Cr^{++})(H^+)(Br^-)$ contributes to the formation of $CrBr^{++}$. Equation 1 then becomes

---

[9] E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

$$\frac{Cr^{+++}}{CrBr^{++}}(Br^-) = \frac{k_1 + k_{H}/(H^+)}{k_{Br^-} + k_{HBr}(H^+)} = \frac{1}{(H^+)}\left[\frac{k_1(H^+) + k_H}{k_{HBr}(H^+) + k_{Br^-}}\right]$$

If, by coincidence, the ratio $k_1/k_H = k_{(HBr)}/k_{Br^-}$, the intercept in a plot such as Fig. 1 would disappear. The *ad hoc* interpretation advanced does not seem particularly attractive in the chemistry it implies, and a more detailed study of the system is required to make it convincing, or to reveal the true cause of the discrepancy.

A study of the type described for Cl^- and Br^- as "catalysts" was not made with F^-, for lack of a simple means of analyzing the products. A series of experiments was performed with F^- and Cl^- present together, observing the success of F^- in winning chromium from the path $k_{Cl^-}(Cr^{++})(Fe^{+++})(Cl^-)$. A decrease in the yield of $CrCl^{++}$ when F^- is present does not prove that the competing path produces CrF^{++}, but this conclusion may be inferred by analogy with the Cl^- and Br^- systems, and with the behavior of the $(NH_3)_5CoX^{++}$ ions. It can be inferred more directly from the observation that the product chromium solution has a marked green color, even when as at high concentration of HF the formation of $CrCl^{++}$ is slight.

The results of the experiments with Cl^- and F^- present simultaneously are shown in Table VI.

TABLE VI

EFFECT OF F^- ON THE FORMATION OF $CrCl^{++}$

Temp. 2.1°, $\mu = 2.2$; $(NaCl)_0 = 0.100$ *M*, $(Fe(ClO_4)_3)_0 = 0.0215$ *M*; $(HClO_4)_0 = 2.06$ *M*; added 2.02 meq. Cr^{++}; volume 200 ml.

HF added	$\frac{(Cr^{+++} + CrF^{++})}{(CrCl^{++})}$	$\frac{(Cr^{+++} + CrF^{++})}{(CrCl^{++})}(Cl^-)$	$(HF)^a$
0.00760	1.09	0.105	0.00295
.0152	1.75	.169	.00683
.0304	3.30	.332	.01695

[a] Calculated assuming $(FeF^{++})(H^+)/(Fe^{+++})(HF) \equiv K_{H^+,FeF^{++}} = 175$, $(FeCl^{++})/(Fe^{+++})(Cl^-) = 1.7$ under the experimental conditions. In the absence of data on the variation of $K_{H^+,FeF^{++}}$ with μ, the value at $\mu = 0.5$ was used[10]; a correction was applied for the change in temperature, following Hudis and Wahl.[11]

For a reaction in which the formation of $CrCl^{++}$ competes with the formation of the aquo ion and of the fluoro ion,[12] the relation expressed by equation 2 follows

$$\frac{(Cr^{+++} + CrF^{++})(Cl^-)}{(CrCl^{++})} = \frac{k_a}{k_{Cl^-}} + \frac{k_{HF}(HF)}{k_{Cl^-}} \quad (2)$$

In equation 2, k_a describes the combined Fe^{+++} and $FeOH^{++}$ paths, and k_{HF} refers to the path expressed by the rate law $k_{HF}(Fe^{+++})(Cr^{++})(HF)$. When the function on the left is plotted against (HF), the data are observed to conform fairly well to a straight line plot. There seems to be no reason to question the validity of equation 2, but the choice of the values for the equilibrium quotients used in calculating the free HF concentration may be in considerable error. A smaller value for the quotient $K_{H^+,FeF^{++}}$ would improve the agreement of the data.

D. Other Systems.—The reaction of Fe^{+++} and I^- is so rapid that a study of the formation of CrI^{++} by the reaction of Fe^{++} with Cr^{++} in the presence of I^- is made very difficult. Ceric ion in excess oxidizes Cr^{++} to $Cr_2O_7^=$.

The reaction of Cr^{++} with oxidizing agents which offer a $2e^-$ oxidation as the initial attack on Cr^{++} have an interest separate from that which guided the work reported here, and will be reported separately.

Discussion

The observations on the reaction of $Co(NH_3)_5Cl^{++}$ with Cr^{++} yield the most definite formulation of the activated complex. It must have an arrangement of the reactant molecules that permits the transfer of chlorine from cobalt to chromium without allowing it to exchange with the solution. In effect, therefore, chlorine must make a bond both with cobalt and chromium in the activated complex, as

$$[(NH_3)_5Co\ldots X\ldots Cr]^{+4}$$

The efficient transfer of electronegative groups which is observed with the other substitution-inert oxidizing agents makes it likely that a similar type of activated complex provides the reaction path in these systems also.

Direct atom transfer, involving again an atom bridge activated complex, is the most reasonable explanation of the observations on the catalysis by Cr^{++} of the dissociation of $CrCl_3$, CrI_3 and $CrCl_2^+$. The reactions for the two types of species may be represented as

$$Cr^*Cl_3 + Cr^{++} \longrightarrow Cr^{*++} + 2Cl^- + CrCl^{++}$$
$$Cr^*Cl_2^+ + Cr^{++} \longrightarrow Cr^{*++} + Cl^- + CrCl^{++}$$

From this formulation it is immediately clear why the systems persist in the well defined stage $CrCl^{++}$ (CrI^{++}), and why little exchange with Cl^- in solution is observed during the reactions. Although reaction may continue involving chlorine transfer between Cr^{++} and $CrCl^{++}$, this process does not affect the stoichiometry and can only be detected by using radioactive chromium as a tracer. The results obtained with the complex cobalt cations showing that attack on Cl is more rapid than on H_2O are preparation for the conclusion that the process

$$(H_2O)_5Cr^*Cl^{++} + Cr^{++} \longrightarrow Cr^{*++} + Cl^- + Cr(H_2O)_6^{+++}$$

will prove to be much slower than

$$(H_2O)_5CrCl^{++} + Cr^{*++} \longrightarrow Cr^{++} + (H_2O)_5Cr^*Cl^{++}$$

The description of the activated complex has stressed the feature of the transfer of an electronegative group in the reactions which were investigated. This emphasis is made only because the observation of the transfer provides the basis for the conclusions about the activated complex which were reached, and is not meant to imply that net atom transfer is an essential part of the electron transfer process. The essential feature is rather that an appropriate bridge provides a more accessible pass for the flow of electrons than does the proton coördination sphere of an ammonated or aquated cation. Whether net transfer of an electronegative group from oxidizing agent to reducing agent takes place depends on the relative substitution lability of the two reactants, and also on the relative substitution lability of the ions left sharing the bridge atom after electron transfer. There is no simple relation between net atom transfer and electron transfer for reactions involving net chemical change. When cobalt(III) complexes react with Cr^{++}, they bring the bridging group into the activated complex because they accept substitution less readily than does Cr^{++}. After electron transfer, Co(II) and Cr(III) are left sharing the bridging group. The shared group is then expected to leave with Cr(III) when the bridge complex is dissociated because Co(II) complexes are known to be more substitution-labile than those of Cr(III). Similarly, when $Fe^{II}_{H_2O}$ and Cr(III) share a bridging group, this is expected to remain associated with Cr(III) on dissociation of the complex. The reaction of Cr^{++} and $Fe(CN)_6^{\equiv}$ is apparently one in which there is no net transfer, but the bridge with CN^- persists in the insoluble product. Fe(II) forms inner orbital complexes with CN^- which are substitution-inert hence the system containing the insoluble product, and the one of the same stoichiometry arrived at by mixing $Cr(H_2O)_6^{+++}$ and $Fe(CN)_6^{\equiv}$ are slow to reach the common equilibrium state. The behavior of the system $Cr^{++} + Fe(CN)_6^{\equiv}$ is intermediate between $Co(NH_3)_5X^{++}$–Cr^{++} and Cr^{++}–$IrCl_6^{=}$. In the one mentioned last, there is no *net* transfer of chlorine to the reducing agent. It is likely, however, that the intermediate green substance which is observed is the bridge complex $(H_2O)_5CrClIrCl_5$. Complexes of Ir(III) are relatively inert to substitution, and when the complex is disrupted, the bridging Cl remains with Ir(III) rather than with Cr(III). These considerations suggest that a system could be selected in which an electronegative atom is transferred from reductant to oxidant on reaction. They furthermore suggest that when a bridged activated complex provides the path for electron exchange in a system in which there is no net chemical change (as for example in electron exchange between Fe^{++} and Fe^{+++}), some transfer of the shared group will always accompany electron transfer. The ion with the charge and electron structure which confers the lower lability will, in the majority of events, take the bridging group into the activated complex, and later out of it. When the electron is transferred, the relative substitution labilities of the ions sharing the bridge are reversed. This point of view makes no prescription as to the direction of atom transfer compared to that of electron transfer. The relation depends on the substitution lability of the reduced form compared to the oxidized form; the lability to substitution of the oxidized form is not necessarily less than that of the reduced form.

---

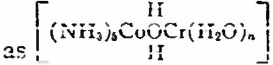
[10] H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949).

[11] J. Hudis and A. C. Wahl, *ibid.*, **75**, 4153 (1953).

[12] If fluoride ion does not add, but merely catalyzes the reaction to form Cr^{+++}, the relation is left unaltered on the right and on the left Cr(III) is shown distributed between Cr^{+++} and $CrCl^{++}$.

The process of electron transfer through bridging atoms in crystalline solids has been discussed by Zener.[13,14] Presumably the role of the bridging atoms for the complexes in solution under discussion is the same, their role being to absorb and deliver the electron transferred. The rates of reaction with Cr^{++} increase in the order $Co(NH_3)_6^{+++}$, $Co(NH_3)_5H_2O^{+++}$, $Co(NH_3)_5Cl^{++}$, $Co(NH_3)_5Br^{++}$. It should be noted that in each of the ions except $Co(NH_3)_6^{+++}$ a pair of electrons is available on the bridging group for interaction with Cr^{++}. The mechanism of reaction with $Co(NH_3)_6^{+++}$ is not known, whether by electron transfer through the proton coördination shell,[15] or by interaction of Cr^{++} with a pair of electrons left unshared when the ion loses a proton. There is also a question about the "bridge" mechanism with $Co(NH_3)_5H_2O^{+++}$ as oxidizing agent, but this will be resolved by oxygen tracer experiments in progress.

The experiment with $Co(NH_3)_5H_2O^{+++}$ oxidizing Cr^{++} in the presence of chloride ion suggests that specific catalysis of electron transfer by negative ions depends largely on their ability to serve as bridges. An activated complex involving Cl^- as a bridge between Co(III) and Cr^{++} is not readily accessible in this system, owing to the reluctance of the Co(III) complex ion to undergo substitution. A slight addition of Cl^- to chromium was observed, however, so that some mode of action besides serving as a bridge must be open for the negative ion. A possibility is a path in which electron transfer in a complex such as



$\left[(NH_3)_5Co\overset{H}{\underset{H}{O}}Cr(H_2O)_n\right]^{+5}$

is consummated by Cl^- substitution on chromium.

In the foregoing it has been assumed that the reactions discussed involve $1e^-$ changes. There is no direct evidence supporting this assumption, but there is a powerful argument against the assumption of a $2e^-$ change. A $2e^-$ change would form the highly unstable intermediate products Cr(IV) and Co(I) with Co(III) as oxidizing agent and Cr(IV) and Fe(I) with Fe(III), and is highly unlikely energetically. Some additional evidence supporting $1e^-$ transfer is comparison with the behavior of systems in which the oxidizing agent is capable of producing a $2e^-$ change. The difference between the reaction of Cr^{++} with Cl_2 on the one hand and Cr^{++} with Br_2 or I_2 on the other may be that with Cl_2 the reaction proceeds at least in part by a primary $2e^-$ change in Cr^{++}

$$Cr^{++} + Cl_2 \longrightarrow CrCl^{+++} + Cl^-$$
$$CrCl^{+++} \rightleftarrows Cr(IV) + Cl^- \text{ (equil.)}$$
$$Cr^{++} + Cr(IV) \xrightarrow{Cl^-} Cr^{+++} \text{ and } CrCl^{++}$$

while with the less powerful oxidizing agents Br_2[16] and I_2 only the $1e^-$ path, which adds halide efficiently, takes place

$$Cr^{++} + X_2 \longrightarrow CrX^{++} + X$$
$$Cr^{++} + X \longrightarrow CrX^{++}$$

A primary $2e^-$ attack on Cr^{++} does not necessarily result in complete transfer; the stage Cr(IV) is probably substitution-labile, and, furthermore, mixed products are to be expected in the reaction of Cr^{++} and Cr(IV). In view of experiments[7] on the exchange between $AuCl_4^-$ and Cl^- induced by Fe^{++}, it is likely that the primary attack of Cr^{++} on $AuCl_4^-$ is also a $1e^-$ change.

The results obtained with the labile oxidizing systems $Fe^{+++} + X^-$ show that with F^-, Cl^- or Br^- present paths involving these ions compete

---

(13) C. Zener, *Phys. Rev.*, **82**, 403 (1951).

(14) The author (H.T.) is grateful to Dr. Sol. Weller for bringing the paper of ref. 13 to his attention.

(15) The analogous system $Co(en)_3^{++}$-$Co(en)_3^{+++}$ studied by W. B. Lewis, C. D. Coryell and J. W. Irvine, *J. Chem. Soc.*, 386 (1949), appears to be a clear-cut example of electron transfer not involving direct atom bridges.

(16) P. R. Carter and N. Davidson (*J. Phys. Chem.*, **68**, 877 (1952)) have proven a $1e^-$ primary process for the reaction of Fe^{++} and Br_2

efficiently with the aquo and hydroxy paths. They have also shown, at least with Br^- and Cl^-, that participation of the halide ion leads to formation of CrX^{++}. One structural feature of the activated complex is therefore made definite; this is that X^- makes bonds to chromium in it. The question of whether the halide also makes a bond to Fe^{+++} is not so definitely settled. We can infer with some confidence that it does, from the observations with the substitution-inert complex ions and from the observation that Cl^- does not catalyze the reaction of $Co(NH_3)_5H_2O^{+++}$ + Cr^{++} appreciably but does have a strong effect on Fe^{+++} + Cr^{++}. The essential difference between the two oxidizing agents is that Fe^{+++} accepts substitution in the first sphere much more readily, and therefore can make use of Cl^- as a bridging group.

The data also lead to the conclusion that there is no important path for catalysis by Cl^- or Br^- which does not involve the formation of a halide–chromium bond in the activated complex. A plausible activated complex for such a path would be one in which Cr^{++} attacks FeX_{aq}^{++} at a water molecule rather than at X. If such a path did contribute, Cr(II) would not be converted completely to CrX^{++} even at high halide but would be distributed between Cr^{+++} and CrX^{++} in the ratio of the halide-catalyzed, non-addition and halide-catalyzed, halide-addition rates. The effect on rate law 1 would be to add a halide-dependent term in the numerator on the right-hand side. In the case of Br^-, the relation is particularly free from the influence of terms in the denominator higher than first power in halide, which might obscure the point at issue, and show that the halide-dependent non-addition path can be at most 5% of the halide addition path. Although terms of higher order do appear in describing the dependence of yield of $CrCl^{++}$ on chloride concentration, thus making it more difficult to assess the importance of an halide-dependent, non-addition path, in this system the path in question must also be a minor one. The results with the substitution-inert oxidizing agents also suggest the conclusion that an oxidizing agent offering both Cl^- and H_2O as point of attack for Cr^{++} is much more vulnerable at the halide group.

It is not clear from the data what products result from the processes corresponding to the higher order terms mentioned for Cl^-, whether, for example, a term $k_{2Cl}(Fe^{+++})(Cl^-)^2(Cr^{++})$ corresponds to the formation of $CrCl_2^+$ alone or of both $CrCl^{++}$ and $CrCl_2^+$. A four-membered ring with two bridging atoms would seem to be a favorable arrangement for an activated complex containing two chlorides, and on this basis any $CrCl_2^+$ formed would have the *cis* arrangement. It is possible that the difference between $CrCl_2^+$ formed by oxidizing Cr^{++} in strong Cl^- medium and that obtained by dissolving green chromic chloride is that one is the *cis* isomer and the other the *trans*.

In Table VII are entered the relative rates at which Cr^{++} reacts with various Fe(III) species. These relative rates have been calculated as implied by equations 1 and 2 from the data of Fig. 1 and Tables V and VI, and depend on the values for equilibrium quotients $K_{FeCl^{++}}$ and $K_{H^+,FeF^{++}}$ cited earlier, as well as the quotients $K_{FeBr^{++}} = (FeBr^{++})/(Fe^{+++})(Br^-) < 0.03$, $K_{FeOH^{++},H^+} = 0.45 \times 10^{-3}$. The estimate of the upper limit for $K_{FeBr^{++}}$ is based on unpublished work[17] which places an upper limit of 0.1 at $\mu = 2$ and 25°, and on the temperature dependence established by Rabinowitch and Stockmayer.[9] The hydrolysis quotient[18] of Fe^{+++} is calculated from the value of 2.5×10^{-3} for $\mu = 2$ and 25°, using the temperature coefficient measured by Rabinowitch and Stockmayer. Table VII also contains the relative rates of electron exchange between Fe^{++} and various Fe(III) species calculated from a compilation of Hudis and Wahl[11], based on their work, that of Silverman and Dodson[19] and Gryder and Dodson.[20]

TABLE VII

RELATIVE RATES OF REACTION OF Cr^{++} WITH Fe(III) SPECIES, AND OF ELECTRON EXCHANGE BETWEEN Fe^{++} AND Fe(III) SPECIES

	Relative rates	
	For Cr^{++} (at 2°, $\mu = 2.2$)	For Fe^{++} (at 0°, $\mu = 0.5$)
Fe^{+++}	1	1
FeF^{++}	3	11.1
$FeCl^{++}$	18	11.1
$FeBr^{++a}$	>100	..
$FeOH^{++}$	2.8×10^3	1.16×10^3

[a] Estimated from the "slope" when the data of Table V are plotted as in Fig. 1.

Accepting the conclusion that the activated complexes involve bridging atoms, the results show the rate of electron transfer from Cr^{++} to Fe(III) complexes to decrease in order with the groups OH^-, Br^-, Cl^-, F^-, H_2O in the bridges. Thus, as for the complexes of Co(III), it appears that a factor other than the distance of approach permitted by the bridge atoms is important in determining the relative rates.

Care must be exercised in drawing conclusions from an array of relative rates such as that shown in Table VII. Since for the systems referred to, equilibrium with respect to complex ion formation is established rapidly, the experimental results yield only the composition of the activated complex, and contain no implication as to the way the activated complex is formed. Table VII shows what the relative specific rates are when we choose to express the rates in terms of the species represented. The choice Cr^{++} + Fe^{+++}, CrF^+ + Fe^{+++}, ..., $CrOH^+$ + Fe^{+++}, equally consistent with the rate law, might yield a quite different order for the efficiency of the bridging groups. When the reactants Cr^{++} + F^- + Fe^{+++}, Cr^{++} + Cl^- + Fe^{+++}, etc., are chosen as the basis for comparison, fluoride appears as the most efficient of the halide ions. If the object is to eliminate from consideration the different tendencies of the ions to associate with the cations and to limit the discussion to the relative rates of electron transfer in the com-

---

(17) A. S. Wilson, Ph.D. Dissertation, Univ. of Chicago, 1950.

(18) A. S. Wilson and H. Taube, THIS JOURNAL, **74**, 3509 (1952).

(19) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(20) J. W. Gryder and R. W. Dodson, THIS JOURNAL, **73**, 2890 (1951).

plexes $[CrXFe]^{+4}$, it is necessary to compare the rates at unit concentration of these species. The data on stabilities to make this comparison possible do not exist. It might be supposed, however, that the complexes would be enough more stable with F^- than Cl^- to reveal a higher specific rate of electron transfer in the chloride bridge complex.

The relative rates shown in Table VII are useful in making comparisons without inquiring into their meaning. The similarity of the relative rates in the two columns suggests that the activated complex involved when Fe^{++} and Fe(III) complexes exchange electrons is of the same type as that for the reaction of Cr^{++} with Fe(III) complexes. Comparison of the activation energies observed for electron exchange between Fe^{++} and Fe(III) complexes with that of substitution on Fe^{++} or Fe^{+++},[21] shows that the rate-determining act is not the substitution to form the bridged activated complex. The energy values are compatible with the assumption that a bridged chemical complex formed as an equilibrium process having ΔH° lower than the activation energy for substitution. If, as seems likely, ΔH° is positive the activation energy for electron transfer in the bridged complex must be small. The low rate for electron transfer in the bridged complex as compared to dissociation of the complex must then be a matter of a much lower temperature-independent factor, *i.e.*, a relatively specific relation of the positions of a large number of atoms is required to make the electron transfer possible.

A condition for a bridged activated complex to provide a more favorable pass for electron transfer than some other process is that at least one of the partners be able to undergo a substitution process readily. Thus although $(NH_3)_6CoH_2O^{+++}$ is inert to substitution, Cr^{++} is labile so that the bridge complex $\left[(NH_3)_5Co\overset{H}{\underset{H}{O}}Cr\right]^{+5}$ can still provide a path for electron exchange. A bridge other than that involving H_2O or OH^- is not readily accessible, however, because this would require substitution on Co(III). On the basis of present information, one cannot be certain that such a substitution may not take place under some labilizing influence of the other reactant, but neither are there any observations which suggest such an influence. Common cations which are fairly labile to substitution[22] and for which bridged activated complexes must be considered for oxidation-reduction or electron exchange reactions in water involving them are: Ti^{++}, Ti^{+++}, Ti(IV), V^{++}, V^{+++}, V(IV), V(V), Cr^{++}, Cr(IV) (?), Mn^{++}, Mn^{+++}, Fe^{++}, Fe^{+++}, Co^{++}, (Co_{aq}^{+++} possibly), Cu^+, Cu^{++}, Ag^+, Ag^{++}, Eu^{++}, Eu^{+++}, Ce^{+++}, Ce(IV), Tl^+, Tl^{+++}. It is admitted that not all electron transfer reactions involve such direct atom bridges. When both partners are substitution-inert and have the coördination spheres blocked, other types of activated complexes are almost certainly involved.

The authors are grateful to Mr. Franz A. Posey, whose skill and diligence in preparing many of the substances used greatly furthered the research. We are also grateful to Dr. E. L. King for valuable discussion of the work, and to the Office of Naval Research for financial support (Contract N6-Ori-02026).

---

[21] J. Bjerrum and K. R. Poulson, *Nature*, **169**, 463 (1952), have measured ~13 kcal. as the activation energy for substitution by CNS of solvent on Fe^{+++}. If the activation energy for substitution on Fe^{++} is similar to that on Ni^{++} and Co^{++}, it is even higher than 13 kcal.

[22] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

CHICAGO 37, ILLINOIS